

Few particles confined in an open pore

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Abstract

This paper presents a modified grand canonical ensemble which provides a new simple and efficient scheme to study few-body fluid-like inhomogeneous systems under confinement. The new formalism is implemented to investigate the *exact* thermodynamic properties of a hard sphere (HS) fluid-like system with up to three particles confined in a spherical cavity. In addition, the partition function of this system was used to analyze the surface thermodynamic properties of the many-HS system and derive both, the *exact* curvature dependence of the surface tension and adsorption, in powers of the density. We use these results to derive for this system the dependence of the fluid-substrate Tolman length up to first order in density.

INTRODUCTION

The thermodynamic and statistical mechanical properties of a fluid composed of many particles confined in small pores have been extensively investigated from both a theoretical and experimental point of view [1–3]. In these systems the fluid fills the cavity inhomogeneously and under extreme conditions, the confinement is responsible for the dimensional crossover of the particles [4]. On the contrary, the knowledge about the statistical mechanical properties of fluid-like systems composed of few bodies is rather poor. Notoriously, few-body systems have played a distinguished role in the development of various fields of physical science including classical, relativistic and quantum mechanics. The fundamental advantage of the few-body systems over the many-body ones obviously resides in that only the former are (in most cases) analytically tractable. In this sense we claim that, the study of few-body systems in the framework of the statistical mechanics of inhomogeneous fluids is interesting because it provides exact solutions in a subject where there are extremely few of such results, thus helping to better understand the properties of many-body systems.

The grand canonical ensemble (GCE), in which the volume, temperature and chemical potential are fixed, is certainly the most used scheme in the formulation of theories of fluids. In particular, the density functional theory (DFT) formulated in GCE, is one of the most successful approaches to properly describe the properties of inhomogeneous fluids. Indeed, DFT calculations make it possible to analyze the adsorption of fluids on substrates and in porous matrices as well as study the interfacial phenomena. Additionally, other theories as the scaled particle theory (SPT) are formulated in the GCE. In this context the hard spheres (HS) systems play an important role in the development of DFT and SPT approaches and in the perturbation theories of fluids [5]. Moreover, HS systems are of particular interest as they constitute a simplified model for both simple fluids and colloidal particles [6].

In this work we present a novel formulation that makes it possible the study of few-body inhomogeneous fluids using a GCE scheme in which the maximum number of particles is considered as a parameter of the system. We employ the proposed GCE to perform an exact study of the HS system with at most three particles confined in a spherical cavity. In addition, on the basis of the new results, we analyze the surface thermodynamic properties of the many-HS system spherically confined. We present our result on the *exact* curvature dependence of surface (or boundary) tension and adsorption, obtained in powers of the

density. The formulation proposed here is found to be a valuable tool for describing highly confined fluids constituted by few bodies. Moreover, it will potentially serve to improve the DFT and SPT descriptions associated with the surface-related thermodynamic properties and their curvature dependence.

PARTITION FUNCTION OF THE FEW BODY OPEN SYSTEM

Consider a one-component fluid containing a non-fixed number of particles which evolve inside a region of the space that we will refer to as \mathcal{B} . Such a region is determined by an external potential $\varphi(\mathbf{r})$ that takes finite values in \mathcal{B} and diverges outside it. The boundary of \mathcal{B} is assumed to be at a constant and uniform temperature T . In these circumstances we expect the fluid will attain an equilibrium state in which its physical properties either remain constant or fluctuate around a fixed value. Furthermore, for an inhomogeneous fluid system in an equilibrium state we assume the following standard hypothesis: i) if the exact expression for the grand canonical partition function (GCPF) Ξ is known, then the exact grand potential function is given by

$$\Omega = -\beta^{-1} \ln \Xi, \quad (1)$$

where $\beta = (k_B T)^{-1}$ is the inverse temperature (with k_B and T being the Boltzmann's constant and the temperature, respectively); and ii) a given thermodynamic property of the system, namely X , is identified with its mean (Gibbsian) ensemble value $\langle X \rangle$. Additionally, it is expected that $\langle X \rangle$ to be equal to its time averaged value over an interval τ , $\bar{X}_\tau = \frac{1}{\tau} \int_\tau X(t) dt$ (at least for a value of τ large enough). Typically, X may be the energy E , the pressure p , the number of particles N , etc. Standard statistical mechanical demonstrations along with usual thermodynamic relations are necessary to compute from the grand potential and its derivatives all of the thermodynamic quantities X [5, 7].

In order to study few-body inhomogeneous systems, we now consider a container \mathcal{B} with at most \mathcal{M} particles, which in what follows will be a fixed parameter. The GCPF of this system is given by

$$\Xi_{\mathcal{M}} = \sum_{j=0}^{\mathcal{M}} \mathcal{I}_j z^j Z_j, \quad (2)$$

where \mathcal{M} is the cutoff value for the maximum number of particles. The factor \mathcal{I}_j is the so-called indistinguishability factor, which is either equal to $\mathcal{I}_j = 1/j!$ for indistinguishable

particles or $\mathbb{I}_j = 1$ for distinguishable particles. In addition, $z = \Lambda^{-3} \exp \beta \mu$ is the activity being $\Lambda = h/(2\pi m k_B T)^{1/2}$ the thermal de Broglie wavelength, while μ , m and h are the chemical potential, the mass of each particle and the Planck's constant, respectively. Finally, The configuration integral (CI) of a system with j particles is

$$Z_j = \int \dots \int \prod e_l \prod e_{lm} d^j \mathbf{r}, \quad (3)$$

being $Z_0 = 1$. Here, $e_l = \exp[-\beta \varphi(\mathbf{r}_l)]$ and $e_{lm} = \exp[-\beta \phi(\mathbf{r}_{lm})]$ are the Boltzmann's factors corresponding to the external and pair interactions, respectively. Note that, the integration domain in Eq. (3) is the complete space due to the spatial confinement of the particles in the region \mathcal{B} is considered in the e_l terms.

In view of the fact that $\Xi_{\mathcal{M}}$ is the GCPF of our system, we can replace in Eq. (1) Ξ with $\Xi_{\mathcal{M}}$ to define Ω . The exact knowledge of Z_j for $1 \leq j \leq \mathcal{M}$ along with Eq. (1) and Eq. (2) provide the exact statistical-thermodynamic properties of the system. In Eq. (2), the expression for $\Xi_{\mathcal{M}}$ is an incomplete (or restricted) version of the usual GCPF obtained from $\Xi = \lim_{\mathcal{M} \rightarrow \infty} \Xi_{\mathcal{M}}$. A different restricted GCE was introduced by Yang and Lee [8] in their study of condensation. It was used later by Woods et al. [9] to study the adsorption of fluids in cavities. We emphasize that in their analysis \mathcal{M} represents the maximum number of particles that fit in \mathcal{B} , instead of an externally imposed parameter as we have assumed in our formalism. An interesting property of $\Xi_{\mathcal{M}}$, Eq. (2), is that for a cavity \mathcal{B} with a fixed size and temperature, $\lim_{z \rightarrow \infty} \Xi_{\mathcal{M}} \propto \mathbb{I}_j z^j Z_j$ with j the maximum number of particles that holds in \mathcal{B} (under the constraint $1 \leq j \leq \mathcal{M}$).

THE FEW HS SYSTEM IN A SPHERICAL CONFINEMENT

Few-body fluid-like systems of HS with one or two particles confined in cavities with different geometries, including the spherical, cuboidal and cylindrical cases, were analytically solved in the canonical ensemble in Refs. [10–12]. That work made it possible to explore on exact grounds the corresponding open systems with $\mathcal{M} = 2$. Further, the three-body HS system was exactly solved for the case of a spherical confinement [13, 14]. In the current work we focus on the study of the HS open system with $\mathcal{M} = 3$ in a spherical cavity. Inhomogeneous systems with a spherical geometry are ubiquitously present in nature in the form of bubbles and drops. One important characteristic of this symmetry is that it

does not place any preferential direction on the space. In spite of the relevance of the spherical geometry much efforts have been directed in recent years towards answering still open questions about the curvature dependence of the thermodynamic properties in spherical systems.

In our description we consider an external hard-wall potential, which is null in a spherical region \mathcal{B} and diverges outside it. The Boltzmann's factor is $e_l = \Theta(R - r_l)$, where $\Theta(r)$ is the Heaviside function, r_l is the distance from the center of the pore to the particle l and R is the effective radius of the pore [13]. The volume of \mathcal{B} is $V = Z_1 = \frac{4\pi}{3}R^3$ and $A = 4\pi R^2$ is the surface area of its boundary. By using the expressions for Z_2 and Z_3 presented in Refs. [10, 13, 14] and assuming indistinguishable particles, i.e., $\mathcal{I}_j = 1/j!$, we obtain the exact expression for Ξ_3 .

Regarding the basic geometrical properties of the spherical confinement we find that, after fixing the diameter of the particles to be $\sigma = 1$ to lighten our notation, a cavity with $R < \frac{1}{2}$ can contain at most one particle, while for the cases $R < \frac{1}{\sqrt{3}} \doteq 0.57735$, $R < \sqrt{\frac{3}{8}} \doteq 0.612372$ and $R < \frac{1}{\sqrt{2}} \doteq 0.707107$, a maximum of two, three and four particles can be fitted in the cavity, respectively. These values imply that by evaluating Ξ_3 we have not only solved the restricted system with $\mathcal{M} = 3$ and any value of R , but also we have obtained the exact solution of the unrestricted system for $R < \sqrt{\frac{3}{8}}$ because in this case $\Xi(R) = \Xi_3(R)$.

The thermodynamic fundamental relations for the grand potential are

$$\Omega = U - TS - \mu N, \quad (4)$$

$$d\Omega = -S dT - P_W A dR - N d\mu, \quad (5)$$

here S is the entropy, dV is equal to $A dR$, P_W represents the (mean) pressure on the wall also called the work-pressure, and $dW = P_W dV$ is the total reversible work performed by the system on its environment. Given that the system is athermal, it is preferable to use temperature-independent quantities like $\beta\Omega$ to conduct the analysis of its properties. By following this argument, some of the usual thermodynamic and statistical mechanical relations for systems under spherical confinement can be written as

$$\beta P_W = -A^{-1} \left. \frac{\partial \beta\Omega}{\partial R} \right|_{\beta, z}, \quad (6)$$

$$\langle N \rangle = N \equiv -z \left. \frac{\partial \beta\Omega}{\partial z} \right|_{\beta, R}, \quad (7)$$

z	0.1	0.2	0.5	1	2	5	10
$\rho_b \times 10$	0.72226	1.1583	1.8962	2.5142	3.1323	3.9028	4.4353
z	20	50	100	200	500	10^3	10^5
$\rho_b \times 10$	4.9217	5.4981	5.8888	6.2452	6.6704	6.9619	8.4313

Table I. Fugacity and bulk-density values used for the curves plotted in Fig. 1.

$$\sigma_N^2 \equiv \langle N^2 \rangle - N^2 = z \left. \frac{\partial N}{\partial z} \right|_{\beta, R}. \quad (8)$$

Here, σ_N is the standard deviation in the number of particles which quantifies the spontaneous fluctuation of N . Since the energy of the system is equal to that of the classical ideal gas, i.e., $\beta U = \frac{3}{2}N$, using Eqs. (4) and (7) we can also calculate S . At this stage, the exact properties obtained for the system are functions of z and R . One important point is the fact that the few-body HS open system is in chemical equilibrium with a bulk HS fluid. Unfortunately, the exact properties of the bulk HS fluid are not analytically known, and thus, to present our results in terms of the bulk density ρ_b (instead of z) we adopt the simple and accurate Carnahan-Starling's equation of state, which for z gives [4, 15]

$$z_{\text{CS}} = \rho_b * \exp \left[\frac{8\eta_b - 9\eta_b^2 + 3\eta_b^3}{(1 - \eta_b)^3} \right], \quad (9)$$

where $\eta_b = \frac{\pi}{6}\rho_b\sigma^3$ is the corresponding packing fraction.

Fig. 1 displays the pressure on the wall as a function of the radius of the cavity, considering different values of ρ_b . Table I summarizes the values of both z and $\rho_b(z)$ used in plotting each curve. These values were derived from Eq. (9). The dashed vertical line in Fig. 1 corresponds to $R = 0.612$, that is, the maximum value for which our results are exact even for the unrestricted system. From this graphic it is evident that the pressure on the wall has a non-monotonous behavior characterized by regions of negative and positive slopes (van der Waals loops), related to the mechanic instability of the system. As a reference, we mention that in the bulk HS system the fluid (disordered) and solid (ordered) stable phases coexist at $\beta P \simeq 11.576$ with fluid and solid bulk-densities $\rho_{bf} \simeq 0.943$ and $\rho_{bs} \simeq 1.041$, respectively [16, 17]. In Fig. 2 we plot the relative adsorption in the pore per unit volume as a function of ρ_b , that is $\Delta\rho = \hat{\rho} - \rho_b$ where $\hat{\rho} = N/V$. There, the arrow indicates increasing values of R . The negative adsorption in the case of the curves corresponding to $R = 1, 1.2$ and 1.5 is a consequence of the cutoff in the maximum number of particles contained in the pore.

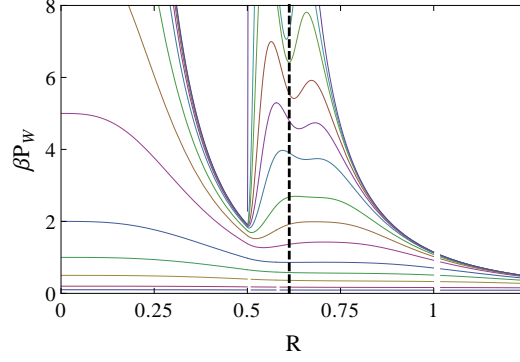


Figure 1. (color-online) Pressure on the wall against the radius of the pore obtained for the values of the bulk density, ρ_b , listed in Table I (ρ_b increases from bottom to top). The dashed line indicates the radius for which a maximum of three particles can be fitted in the cavity.

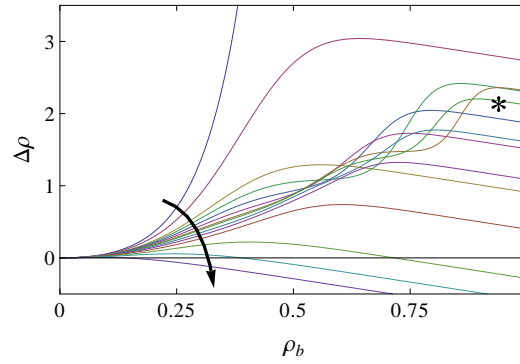


Figure 2. (color-online) Relative adsorption in the pore as a function of the bulk density plotted for different radii of the pore $R = 0.2, 0.4, 0.5, 0.525, 0.55, 0.575, 0.6, 0.61237, 0.65, 0.7, 0.8, 1, 1.2$, and 1.5 . The arrow marks the direction of increasing values of R . The asterisk indicates the curve for $R = 0.61237$.

The same conclusion applies to the negative slope region for $R = 0.65, 0.7$ and 0.8 . Fig. 3 shows the filling of the cavity as a function of ρ_b for different radii of the pore. In this plot the saturation value of N corresponding to each value of R coincides with the maximum number of particles (at most three) that holds in the pore. As it can be observed, $N(\rho_b, R)$ is a non-decreasing function. It is noticeable that for $0.5 < R < 0.61237$ the curves change their concavity several times with the increase of ρ_b . This property determines the behavior of $\sigma_N^2(\rho_b)$ through Eq. (8). Fig. 4 illustrates the relation between the mean number of particles in the cavity and its fluctuation σ_N . We find that the curves corresponding to

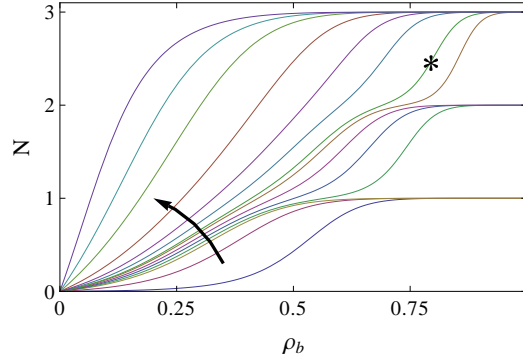


Figure 3. (color-online) Mean number of particles vs. bulk density for different radii of the pore. The arrow, the asterisk and the values of R were described in Fig. 2.

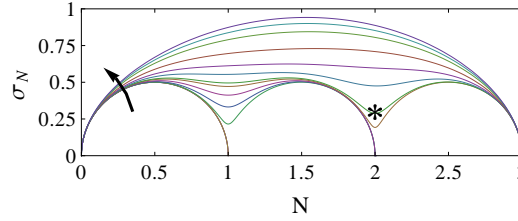


Figure 4. (color-online). Standard deviation in N as a function of N for different radii of the pore. The arrow, the asterisk and the values of R were described in Fig. 2.

$R < 0.5$ collapse onto the semi-circle centered at $N = 0.5$. For $0.5 < R < 0.577$ and $1.5 < N \leq 2$ the curves collapse onto the second semi-circle centered at $N = 1.5$, while for $R > 0.577$ and $2.5 < N \leq 3$ the curves collapse onto the third semicircle. In addition, we have analyzed the case $\mathcal{M} = 2$ and obtained a picture (the graphic is not shown here) similar to that displayed for the case $\mathcal{M} = 3$ but with two semicircles centered at $N = 0.5$ and $N = 1.5$. One important consequence of the graphic showed in Fig. 4 is that it can be straightforwardly extended to obtain the representation for the case with a value of $\mathcal{M} \geq 3$. Basically, it will involve a sequence of \mathcal{M} semicircles of unit diameter centered at half-integer values of N along the abscissa axis. In particular, for a given R the curve will start at the origin $(N, \sigma_N) = (0, 0)$, and will collapse either onto the semicircle that ends at the value N equal to the maximum number of particles that fit in this cavity or onto the \mathcal{M} -th semicircle in case R is large enough. It is to be noted that, the outmost curve which connects $N = 0$ to $N = \mathcal{M}$, can be obtained analytically.

THE MANY HS SYSTEM IN CONTACT WITH A SPHERICAL WALL

In what follows we draw attention to the implications that the expression for Ω , obtained for the system with $\mathcal{M} = 3$, has on the surface-thermodynamic properties of the many-body system. In particular, we will address on the HS system in contact with a hard spherical wall in the low density limit. For each magnitude of the system, our main goal is to find its *exact* power series in ρ_b up to the three bodies term, where the dependence on the curvature is included in the coefficients of the series. Our procedure is based on the ideas developed in Ref. [12], which enable us to express the $Z_i(R)$ terms analytically known, as a function of the set of measures $\{V, A, R\}$. We begin by placing the dividing surface at R and we use the same decomposition rule adopted in Ref. [13] (Eqs. (28) and (29) therein). For the unknown Z_i terms we assume a generic dependence $Z_i(V, A, R)$. As a result, we obtain an expression for Ω as a function of V, A, R and z . We then fix $\mathcal{M} = 4$ in Eq. (2) and calculate the magnitude X . We expand the expression for X as a power series in the variable ρ_b by following standard procedures based on the inversion and composition of the power series. Then, we truncate the series to the first term in which Z_4 appears. In addition, to obtain the planar-surface property we consider the limit of the series as $R \rightarrow \infty$. Thus, we determine in the planar limit the expressions for the fluid-substrate surface-tension $\gamma \equiv \partial\Omega/\partial A|_{V,R}$ and the adsorption per unit area $\Gamma \equiv V(\hat{\rho} - \rho_b)/A$,

$$\beta\gamma_\infty = -\frac{\pi}{8}\rho_b^2 \left(1 + \frac{149\pi}{210}\rho_b\right) + O(\rho_b^4), \quad (10)$$

$$\Gamma_\infty = \frac{\pi}{4}\rho_b^2 \left(1 - \frac{113\pi}{420}\rho_b\right) + O(\rho_b^4). \quad (11)$$

Eq. (10) exactly reproduces the first two terms (the only known up to present) of the series expansion of $\beta\gamma_\infty(\rho_b)$. The above Eqs. are consistent with the Gibbs adsorption isotherm $\Gamma_\infty = -\partial\gamma_\infty/\partial\mu$. Moreover, Eq. (10) and Eq. (11) are in close agreement both with simulation results up to a moderate density $\rho_b \simeq 0.4$ (see [18]) and theoretical results obtained using SPT (see Figs. 2 and 3 in [19]). As is well known, the important problem in statistical mechanics regarding the dependence of the surface thermodynamic properties on the curvature remains unresolved, even for the HS fluid in contact with hard spherical walls. Following the procedure described above and writing the magnitude X/X_∞ as a double

power series in the variables R^{-1} and ρ_b , we obtain

$$\gamma(R)/\gamma_\infty = 1 + \delta_\infty 2R^{-1} + \delta_k R^{-2} + O(R^{-3}), \quad (12)$$

$$\Gamma(R)/\Gamma_\infty = 1 + \xi_j 2R^{-1} + \xi_k R^{-2} + O(R^{-3}). \quad (13)$$

We included in the appendix the complete expression for $\gamma(R)$ and $\Gamma(R)$ in the limit of both small ρ_b and large R . In the latter equations, $2R^{-1}$ and R^{-2} are the mean and Gaussian curvatures of the spherical cavity, respectively. The coefficient δ_∞ denotes the radius-independent wall-fluid Tolman length. In fact, neither of the coefficients in the latter two equations depends on R . We verified that Eq. (12) and Eq. (13) hold for fluids in contact with a hard spherical wall, irrespective of whether the fluid is inside the cavity ($R > 0$) or outside of a fixed hard sphere ($R < 0$, also known as an empty cavity in a bulk fluid) [13]. To first order in density the coefficients δ_∞ and δ_k can be computed from

$$\begin{aligned} \delta_\infty &\doteq 0.34299 \rho_b, \delta_k \doteq -0.05555 + 0.19933 \rho_b, \\ \xi_j &\doteq 0.51448 \rho_b, \xi_k \doteq -0.05555 + 0.29899 \rho_b. \end{aligned} \quad (14)$$

No numerical simulation results have been published up to present for these magnitudes. The expressions for both δ_∞ and δ_k determined by the above procedure are consistent with those recently reported in [13], derived from an exact calculation for a few-body system treated in the framework of the canonical ensemble. In addition, Siderius et al. [19] evaluated δ_∞ by using six different versions of SPT (see Fig. 5 in Ref. [19]). From the comparison between their and our results we find that only the expression for δ_∞ obtained by using the CS-SPT version is compatible with the low density behavior presented here in Eq. (14). Indeed, in Ref. [19] it is shown that the E-SPT version gives a value $\delta_\infty(\rho_b = 0) \neq 0$ [20], while the others SPT versions yield slopes that differ by a factor of about three from the exact value derived from Eq. (14). At this point, we must note that the dependencies of γ and Γ on the curvature [Eqs. (12-14)] strongly depend on the details of the procedure by which they were obtained [12, 13] as well as on the choice for the location of the dividing surface. Further details regarding the present treatment will be discussed elsewhere. It is important to emphasize that the thermodynamic limit was not invoked in our calculations of the properties of the many-body system. Moreover, although the z_{CS} equation of state given in Eq. (9) is used in the actual calculations, it does not introduce any approximation

in Eqs. (10-14) due to z_{CS} is exact to the order of the three-body term involved in our results.

In summary, we presented a restricted GCE form, which is specially useful for analyzing the statistical mechanical properties of few-body open systems. We used the partition function of this restricted ensemble to evaluate, in an exact analytical framework, several properties of the HS fluid-like system composed of at most three particles. Additionally, we extended our analysis to derive the surface thermodynamic properties of the many-body system of HS in contact with a hard spherical wall. By adopting a power series representation we reported new expressions for both the surface tension and adsorption, as a function of the density and curvature. We use these results to determine the Tolman length of the fluid-substrate system.

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APPENDIX

The complete expressions for $\beta\gamma$ and Γ

$$\beta\gamma = \left(a_2 - \frac{c_{2k}}{R^2}\right) \rho_b^2 + \left[a_3 + \frac{8}{3}\pi a_2 - \frac{2c_{3j}}{R} - \frac{3c_{3k} + 8\pi c_{2k}}{3R^2}\right] \rho_b^3,$$

$$\Gamma = \left(-2a_2 + \frac{2c_{2k}}{R^2}\right) \rho_b^2 + \left[-\frac{9a_3 + 16\pi a_2}{3} + \frac{8c_{3j}}{R} + \frac{9c_{3k} + 16\pi c_{2k}}{3R^2}\right] \rho_b^3,$$

$$\text{with } a_2 = -\frac{\pi}{8}, a_3 = \frac{137\pi^2}{560}, c_{2k} = -\frac{\pi}{2^4 3^2}, c_{3j} = \frac{9\pi\sqrt{3+16\pi^2}}{1536}, c_{3k} = \frac{781\pi^2}{36288}.$$

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